



Identification and remediation of sulfation in lead-acid batteries using cell voltage and pressure sensing

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HIGHLIGHTS

- ▶ Real-time aging diagnostic tools were developed for lead-acid batteries using cell voltage and pressure sensing.
- ▶ Different aging mechanisms dominated the capacity loss in different cells within a dead 12 V VRLA battery.
- ▶ Sulfation was the predominant aging mechanism in the weakest cell but water loss reduced the capacity of several other cells.
- ▶ A controlled-pressure charging algorithm was designed and applied to reverse sulfation in the weakest cell.
- ▶ Desulfation increased the sulfated cell capacity by 41% and the battery capacity by 25%.

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ABSTRACT

The operating environment, manufacturing variability, and use can cause different degradation mechanisms to dominate capacity loss inside valve regulated lead-acid (VRLA) batteries. If an aging mechanism for each cell can be identified in real-time, cell usage can be adjusted by the battery management system to optimize the performance and service life of the energy storage system. In this paper, the cell voltage and pressure of new and dead VRLA batteries are monitored during testing to determine the cause of death of the cells. The new cells have fairly uniform performance with limited signs of degradation while the cells in the dead battery have widely ranging performance, especially at the end of discharge and charge. Based on the measurement data, it appears that one cell died from sulfation and another three died of dehydration. The battery capacity is mainly dictated by the sulfated cell. A desulfation charging control scheme with pressure feedback is designed to break up hard sulfate and recover capacity while minimizing water loss by using low current charging. The capacity of the cell is recovered by 41% with minimal water loss, demonstrating the effectiveness of the desulfation charge controller.

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1. Introduction

Lead-acid is the most widely used chemistry for batteries in stationary and hybrid applications, with the majority consisting of a valve-regulated lead-acid (VRLA) design. The most common damage mechanisms for a VRLA battery include [1–9]:

- Positive electrode corrosion
- Irreversible hard sulfation
- Water loss/dry-out
- Positive electrode softening and shedding
- Electrolyte stratification

- Internal short-circuit
- Mechanical damage (current connector failure, case damage, etc.)
- Others (passive lead oxide film, thermal runaway, etc.)

They are often not independent from each other and multiple mechanisms can occur in one cell. VRLA batteries are designed to minimize these effects as much as possible but the operating environment, cell-to-cell and battery-to-battery manufacturing variations, and use can cause different degradation mechanisms to dominate capacity loss and/or impedance rise. With the ability to determine in real time the predominant degradation for each cell, battery management system (BMS) can predict the cell SOH accurately, adjust cell use accordingly and balance cells with respect to their health conditions so as to extend service life of the battery pack.

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For system/control engineers, a practically optimal BMS design will have a very accurate yet computationally cheap baseline model, as fewer as possible sensors, and sophisticated controllers. The controllers use the model and the sensor measurements (e.g., current, voltage, temperature, etc.) to calculate/estimate the other states (e.g., state of charge, state of health), predict the future performance based on the external power demand (e.g., how much power and how long the pack can provide it, how much life will be left and when maintenance will be needed) so that the BMS can adjust the cells use, protect the cells from thermal runaway and other safety issues, balance the cells according to not only SOC but also SOH, maintain their service lives, and optimize the overall pack performance.

There are several challenges here. First, to have accurate estimation of SOC/SOH requires an underlying model including the predominant aging mechanisms but usually such a comprehensive model is complicated and computationally so expensive that it cannot be handled by a small on-board microprocessor. Second, more sensors make it easier for system engineers to design high performance controllers. Given the limited space within the pack and the large number of cells, it is typically not practical to have the detailed measurements that can be made in a laboratory setting. Third, in industrial applications, many manufacturing parameters such as acid concentration, saturation, and grid composition, needed for controllers design are not available due to IP agreements or contracts which drives engineers to add extra on-board sensing or use estimators based models.

To perform real-time aging diagnosis in vehicles/locomotives, nondestructive techniques with as few sensors as possible are favored because switching out an aged cell from a pack and examining it using laboratory tools/methods costs a lot of labor and system downtime and can only be performed at very low frequency. Many studies that investigate aging in VRLAs use destructive techniques to identify degradation mechanisms. Studying a dissected battery using a scanning electron microscope and chemical analysis provides a physical understanding of aging processes, such as hard lead sulfate formation [10–12] or corrosion layer growth [13,14]. Although these invasive techniques provide detailed information about the SOH of the battery, they can only be used posthumously. With nondestructive monitoring techniques, on the other hand, the BMS can diagnosis aging and implement unique charging strategies to extend service life.

Nondestructive techniques are also essential for accurate SOH estimation in real time. Most nondestructive techniques for on-line SOC/SOH estimation are model-based [15–18] and require accurate model fitting. The techniques developed so far, however, do not specify the degradation mechanisms that cause battery aging or use models which require a priori knowledge of major degradation. Trying to include every possible failure mode in the model can result in computationally-expensive models that on-board BMS cannot handle. Analyzing data from nondestructive tests may offer an alternative to a model-based approach for SOH estimation. Nondestructive tests that require only current and voltage data include: full charge/discharge cycling, pulse train, and Electrochemical Impedance Spectroscopy (EIS). In particular, EIS is influenced by SOC [19] and the shape of the impedance curve is often related to degradation mechanisms, such as gassing at a single electrode [20].

In this study, individual cell voltage and pressure measurements are available and the current can be controlled to completely charge/discharge, pulse train, and sinusoidally charge/discharge for EIS. These are considered to be nondestructive measurements because the access terminals and pressure ports could be integrated relatively easily into the battery. Voltage and pressure sensors are attached during the autopsy to make the desired measurements.

The results of this autopsy can then be used to revive the battery, adjust the BMS utilization, or direct recycling efforts.

The ability to not only identify degraded cells within a VRLA battery but also to restore their capacity could dramatically prolong battery life. Typical VRLA batteries have multiple cells connected in series. As the battery ages, the cell capacities diverge and the cell with the lowest capacity limits the overall battery capacity. A BMS that identifies sulfated cells and has the ability to desulfate those cells could increase the overall capacity of an aged battery.

Negative plate sulfation is one of the most prominent aging mechanisms for VRLA batteries and is especially common in hybrid vehicle applications [21,22]. Gibson et al. conclude that high rate charging and discharging at partial states of charge leads to the progressive accumulation of lead sulfate on the negative plates of VRLA batteries. Gibson et al. [10], Yamaguchi et al. [11], and Takehara [12] have thoroughly studied and developed an understanding of the structure and recrystallization of hard crystalline lead sulfate. Lead dioxide and lead are discharged in sulfuric acid to form lead sulfate and water. The reaction reverses during charge, lead sulfate being decomposed to produce lead dioxide and lead. Both reactions take place via dissolution–precipitation processes. During discharge, electrons are transferred to form lead ions then dissolved into the solution and supersaturation of Pb^{2+} may be achieved. After the nuclei are formed, $PbSO_4$ precipitates and the size of the $PbSO_4$ crystals depends on the concentration of sulfuric acid and the current density. During charge, lead sulfate dissolves into Pb^{2+} and SO_4^{2-} . Then electron transfer occurs on the electrode grid and the ions are oxidized/reduced to PbO_2 and Pb. This process is greatly affected by the current density, the diffusion rate, the crystal size and the solubility of $PbSO_4$. In addition, the reaction area changes by several orders of magnitude during the reactions. The lead sulfate crystals formed through electrochemical process have rough surfaces with high porosity and activity. Therefore, the lead ions may dissolve from the crystals and re-crystallize back, a process known as Ostwald ripening. Crystals formed in recrystallization have finer surfaces with higher density and lower activity. Hence, these lead sulfate crystals have less reaction area and are much more difficult to be converted back during charge. Approaches to reducing sulfation include high-frequency pulse charging [23,24], using carbon additives [25,26] and expander components [8,27,28] and replacing the negative electrode with carbon [21,29,30].

Desulfation can restore some of the capacity lost to sulfation. Most commercial battery chargers/desulfators conduct desulfation using a technique known as “pulse conditioning”, which consists of applying short, high-current pulses to a cell [31–34]. Lam et al. found pulsed charging to be a promising approach towards enhancing the cycle life of Pb–Sb and Pb–Ca–Sn cells [35] that Keyser et al. proposed to use high finishing currents and current-interrupt charging algorithm to minimize sulfation and gassing during cycling [36]. Hydrogen and oxygen production associated with the electrolysis of water molecules at high states of charge, however, can lead to water loss, another aging mechanism that decreases cell capacity. Desulfation techniques must minimize water loss to effectively recover lost capacity.

Electrolyte stratification is another common failure mode for lead-acid batteries. It is considered to be most severe in flooded batteries, much less prominent in AGM batteries and not significant at all in gelled batteries due to the immobilized electrolyte [37–39]. Electrolyte stratification causes a vertical distribution of acid and promotes the formation of irreversible lead sulfate in the lower parts of the electrodes [40,41]. Electrolyte stratification can be mitigated by overcharging and gassing [9,39,40,42].

The goal of this work is to develop real-time aging diagnostic techniques that can be integrated into battery management

systems (BMS) to improve online state of health (SOH) estimation accuracy. Therefore, the methods should be nondestructive/non-intrusive (without opening the pack and cells), simple and cheap (use as few sensors, electronics, and supporting hardware as possible). There are electrochemical laboratory methods (such as using SEM and AFM) that are simple and provide conclusive results in determining cell degradation. These are not practical for online/real-time usage because they require special equipment, skilled technicians and opening the battery which results in a lot of labor cost and system downtime. This motivates the approaches taken in this paper to find other ways to determine the most likely degradation mechanisms in lead-acid batteries that can be implemented online in real-time at low cost.

In this study, a dead AGM VRLA battery is compared to a new battery of the same make and model. The dead battery was cycled over the course of several months on an Arbin BT2000 using a switchyard cycle. Each battery consists of six chambers connected in series (see Fig. 1) containing eighteen cells in parallel. The test results are used to diagnose the dead chambers and their cause of death. Since the 18 cells in parallel in each chamber were not differentiated in this study and their total voltage is the same as that of a single Pb-acid cell, they are referred to as cells in this paper. After identifying the dominant aging mechanisms, a charging algorithm is designed and implemented to revive one of the dead cells in order to increase the overall capacity of the battery.

2. Nondestructive aging diagnosis

2.1. Experimental setup

The dead battery was cycled on an Arbin BT2000 for 31,560 cycles using a duty cycle representative of an electric locomotive operating an 8-h shift in a switchyard. The duty cycle was a low-rate partial-state-of-charge cycle and consisted of 80 small pulse discharge/charge cycles and a constant-current–constant-voltage (CC–CV) charge at the end of the shift. The battery was declared dead when the capacity fell to approximately half of its initial value.

In addition to the dead battery, a new battery was procured and used as a control. The measured capacities of the new and dead batteries were 70 Ah and 40 Ah, respectively. An AE Techtron LVC 5050 linear amplifier, dSPACE DAQ system, and additional custom-built hardware were integrated together and used to conduct cycling, pulse-train, and EIS testing (see Fig. 2). Five rods were threaded to a depth of approximately 0.0127 m (0.5 inches) into the top of each current collector without damaging the battery shield seal so that individual cell voltages could be measured without

pressure leakage during testing. Holes were drilled into each individual cell and tubes were inserted and sealed to enable pressure measurement (see Fig. 3). Omega PX309 pressure transducers were attached to the tubing and electrically connected to dSPACE to measure the cell pressures. These transducers are capable of measuring gauge pressures ranging from 0 to 34.47 kPa (from 0 to 5 psi) with 0.25% accuracy. Before recording data, the offset error of each gauge pressure transducer is removed in software. An additional absolute pressure transducer measures atmospheric temperature. A National Semiconductor LM34 measures room temperature.

The valves on the battery lid were tested to open between 13.77 and 20.68 kPa (2–3 psi) using compressed air and a pressure gauge. The tubing from the battery to the pressure transducers was sealed and tested to ensure no observable leakage. In addition, the entire system was pressurized to 13.77 kPa (2 psi), less than the valve opening pressure, and monitored for 24 h to detect any slow leakage and pressure variation due to temperature and ambient pressure change.

During full charge/discharge testing, the batteries were discharged from 100% SOC until a cutoff voltage of 10 V was reached. The batteries were rested for at least 24 h and then charged to 100% SOC using a CC–CV charging profile. The CC current was 0.1 C and the CV termination was 15 V.

EIS is to show the battery impedance spectrum over a frequency range. It is the same as Nyquist plot used control engineers. Both tests perform by giving sine waves with different frequency to the system, i.e. battery here, and measuring the voltage responses to calculate the resistances of the system. Battery impedance was measured using the Frequency Response Analyzer (FRA) method, in which a small sinusoidal battery voltage and the current response are the input and output of the system, respectively [43]. The small cell voltage signal passes through an external circuit that removes the DC offset (i.e. the battery open-circuit voltage, OCV) and amplifies the remaining AC signal. A DAQ system then reads the level-shifted and amplified voltage signal. The external circuitry ensures that the voltage signal spans the full range of the analog to digital input channel. This reduces quantization error, which improves signal quality and reduces noise in EIS plots. Current was measured using LEM CASR-6NP hall-effect transducers with an accuracy of 48 mA.

Since battery impedance is very small (on the order of mΩ), only a 10 mV battery voltage signal was necessary for producing a substantial current response. The frequency of the battery voltage signal was held constant for five cycles at logarithmically spaced points between 0.01 Hz and 100 Hz. FFTs were used to analyze the voltage and current signals. Impedance was then calculated from amplitude and phase data. The test circuit was validated using a Solartron SI1255B Frequency Response Analyzer on an A123 Lithium-Ion cell [44].

2.2. Aging mechanisms identification

The cell voltage plot in Fig. 4(e) shows that Cell #3 experiences a rapid decrease in voltage after 50% depth of discharge (DOD). The other five cells have relatively normal discharge curves and could provide significantly more charge if not for the reduction in battery voltage caused by Cell #3. Therefore, Cell #3 had the lowest capacity which also dictated the capacity of the battery.

Given that Cell #3 did not suffer severe gassing during charge (no pressure and voltage rise shown in Fig. 5(b) and (e)), Cell #3 is possibly dead from hard sulfation or corrosion. Irreversible hard sulfation refers to the hard crystallization of lead sulfate via recrystallization process, which causes part of the products of discharge cannot be reused and decomposed in charge and results

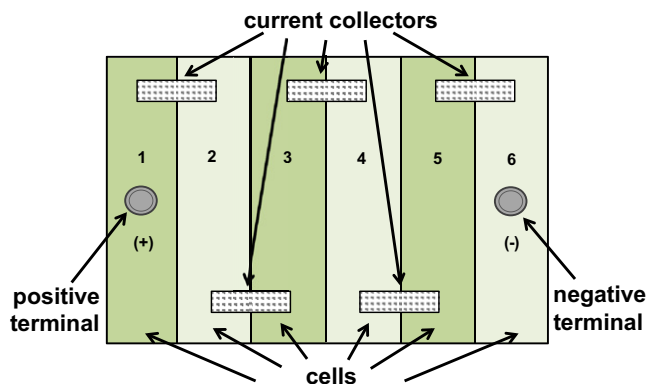


Fig. 1. VRLA battery configuration: 6 cells in chambers 1–6 are individually sealed and connected in series through current collectors.

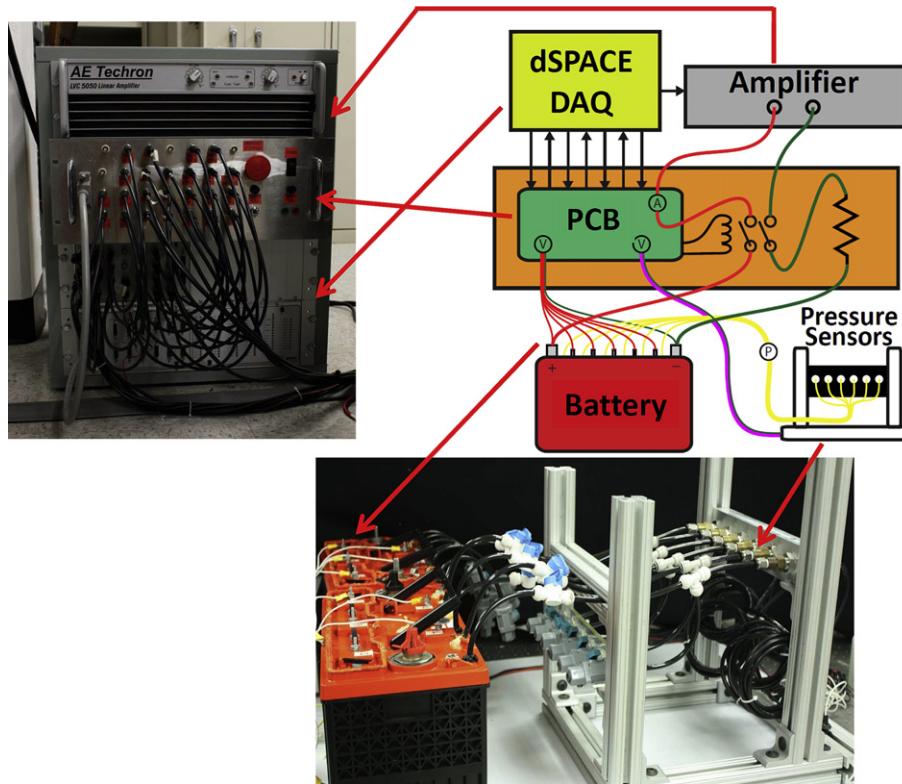


Fig. 2. Diagram of the testing hardware.

in loss of active material and thus, capacity. When hard sulfation occurs, the effective specific surface area will be reduced and the internal acid concentration will be lowered. Corrosion is a process that the electrode grid is oxidized and the layer of the oxidation products prevent the current flux to go through, resulting in impedance rise, but no direct effect on the internal acid concentration. For Pb-acid batteries, the internal acid concentration is reflected by the open circuit potential (OCV) [45]. As shown in Fig. 6, the OCV is a monotonically increase function of the acid concentration. Therefore, the lower initial OCV of Cell #3 in Fig. 4(g) is an indicative of hard sulfation. The combination of pulses of charge/discharge and long-term parasitic load in the duty cycles which aged the battery, provides friendly environment for hard sulfation. This is also indicative of hard sulfation as the prominent cause of death of Cell #3.

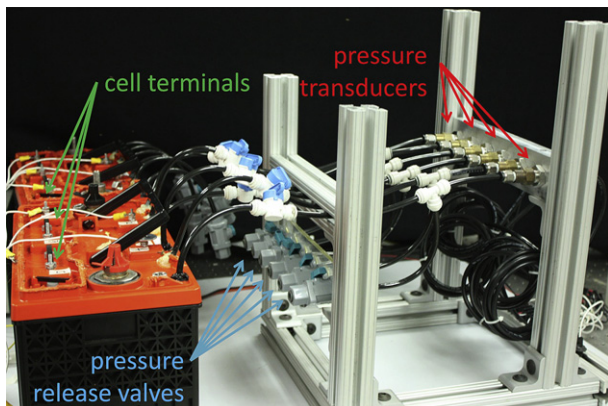


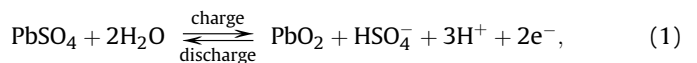
Fig. 3. Photograph of the experimental setup.

3. Desulfation and capacity recovery

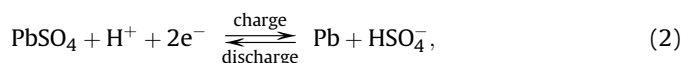
The test results identify sulfation in one cell and water loss in three cells as probable degradation mechanisms. The capacity of the dead VRLA battery was limited largely by sulfation in one of six cells. A desulfation/charging algorithm is developed to increase the capacity of the sulfated cell without causing water loss. The algorithm charges only the sulfated cell while using cell pressure feedback control to minimize gas generation. Successful desulfation validates the diagnosis of sulfation in Cell #3 as the primary aging mechanism because corrosion is irreversible.

3.1. Gas evolution during overcharge

Optimal desulfation requires charging a cell with as much current as possible without crossing the voltage threshold that induces excessive gassing. The primary reaction in the positive electrode of a Pb-acid battery is



where the standard electrode potential $E_{\text{PbO}_2/\text{PbSO}_4}^0 = 1.636$ Vvs. SHE. The primary reaction in the negative electrode is



where $E_{\text{Pb}/\text{PbSO}_4}^0 = -0.295$ Vvs. SHE. The overall cell potential is $E_{\text{cell}}^0 = E_{\text{PbO}_2/\text{PbSO}_4}^0 - E_{\text{Pb}/\text{PbSO}_4}^0 = 1.931$, but the actual cell potential E_{cell} depends on acid concentration, according to the Nernst equation [46],

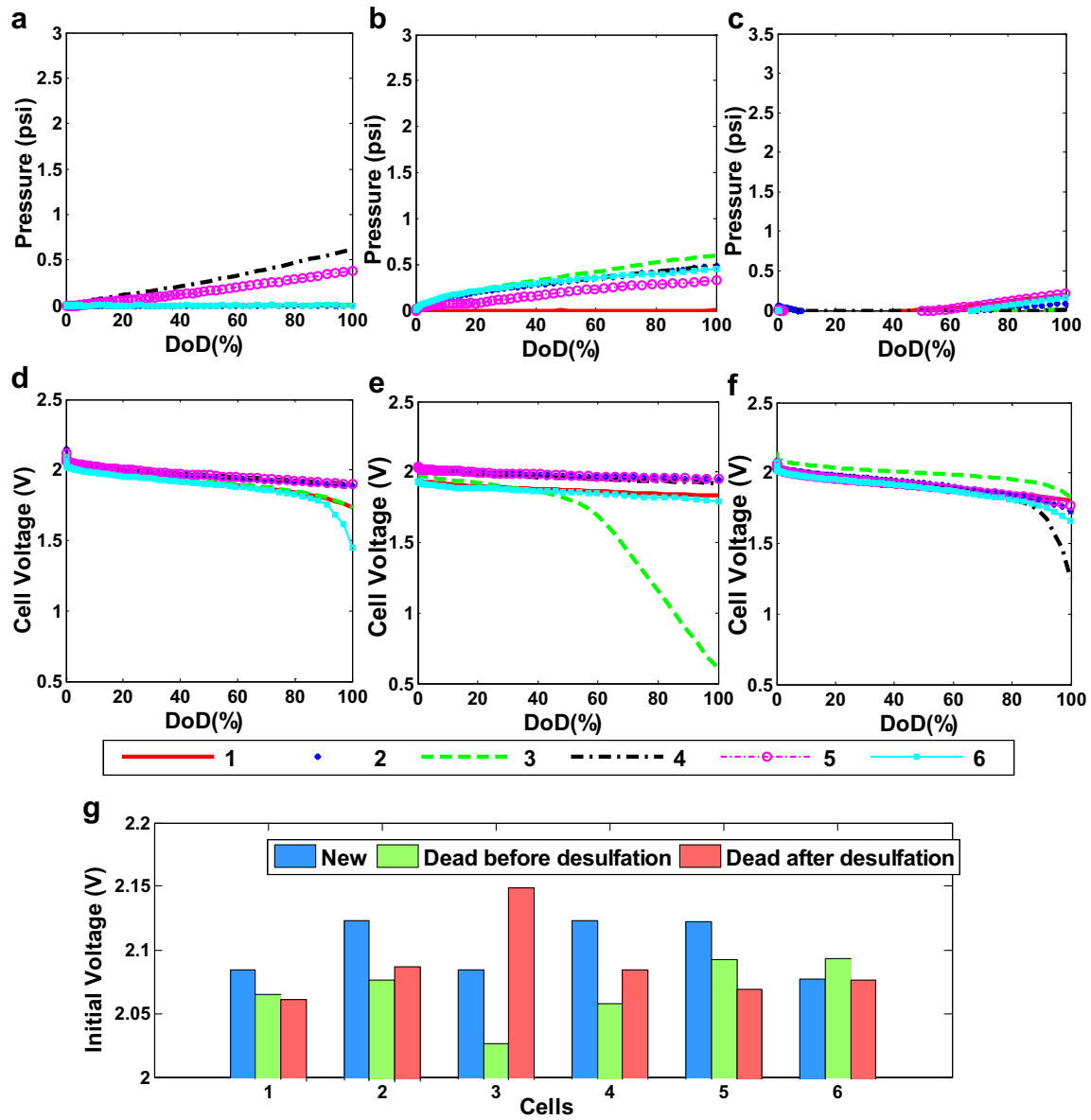


Fig. 4. Discharge of the new and the dead batteries: (a) cell pressure of the new battery; (b) cell pressure of the dead battery before desulfation; (c) cell pressure of the dead battery after desulfation; (d) cell voltage of the new battery; (e) cell voltage of the dead battery before desulfation; (f) cell voltage of the dead battery after desulfation; (g) Initial cell voltages of the new and the dead batteries before and after desulfation. (1 psi = 6.8948 kPa).

$$E = E_{\text{cell}}^0 + \frac{RT}{nF} \ln \left(\frac{a_{\text{H}^+} \cdot a_{\text{HSO}_4^-}}{a_{\text{H}_2\text{O}}} \right), \quad (3)$$

where $R = 8.314 \text{ J Kmol}^{-1}$ is the universal gas constant, $F = 9.64810^{-4} \text{ C mol}^{-1}$ is Faraday's constant, T is the temperature in degrees K, n is the number of moles of electrons transferred and $a_{\text{H}_2\text{O}}$, a_{H^+} , and $a_{\text{HSO}_4^-}$ are the reactant concentrations.

During charging, oxygen evolves at the positive electrode,



at the water decomposition voltage $E_{\text{O}_2}^0 = 1.23 \text{ V}$ vs. SHE and hydrogen recombines,



Hydrogen also evolves at the negative electrode,



at $E_{\text{H}_2}^0 = 0 \text{ V}$ vs. SHE and oxygen recombines



Oxygen evolution occurs when the positive electrode potential is above $E_{\text{O}_2}^0$ and hydrogen evolution occurs when the negative electrode potential is below $E_{\text{H}_2}^0$. Similarly, oxygen and hydrogen recombination occur when the electrode potentials are below $E_{\text{O}_2}^0$ and above $E_{\text{H}_2}^0$, respectively. The electrode potentials of a Pb-acid battery exceed the gas production thresholds ($E_{\text{Pb/PbSO}_4}^0 < E_{\text{H}_2}^0$ and $E_{\text{PbO}_2/\text{PbSO}_4}^0 > E_{\text{O}_2}^0$), so hydrogen and oxygen continually evolve during charging. Thus, these secondary reactions are unavoidable [45] but the gas generation rates can be extremely small if the overpotential voltage is not too large. The gas evolution rate increases exponentially with voltage above and below $E_{\text{O}_2}^0$ and $E_{\text{H}_2}^0$, respectively.

Oxygen that has been generated at the surface of the positive electrode passes through gas paths in the AGM separator to the

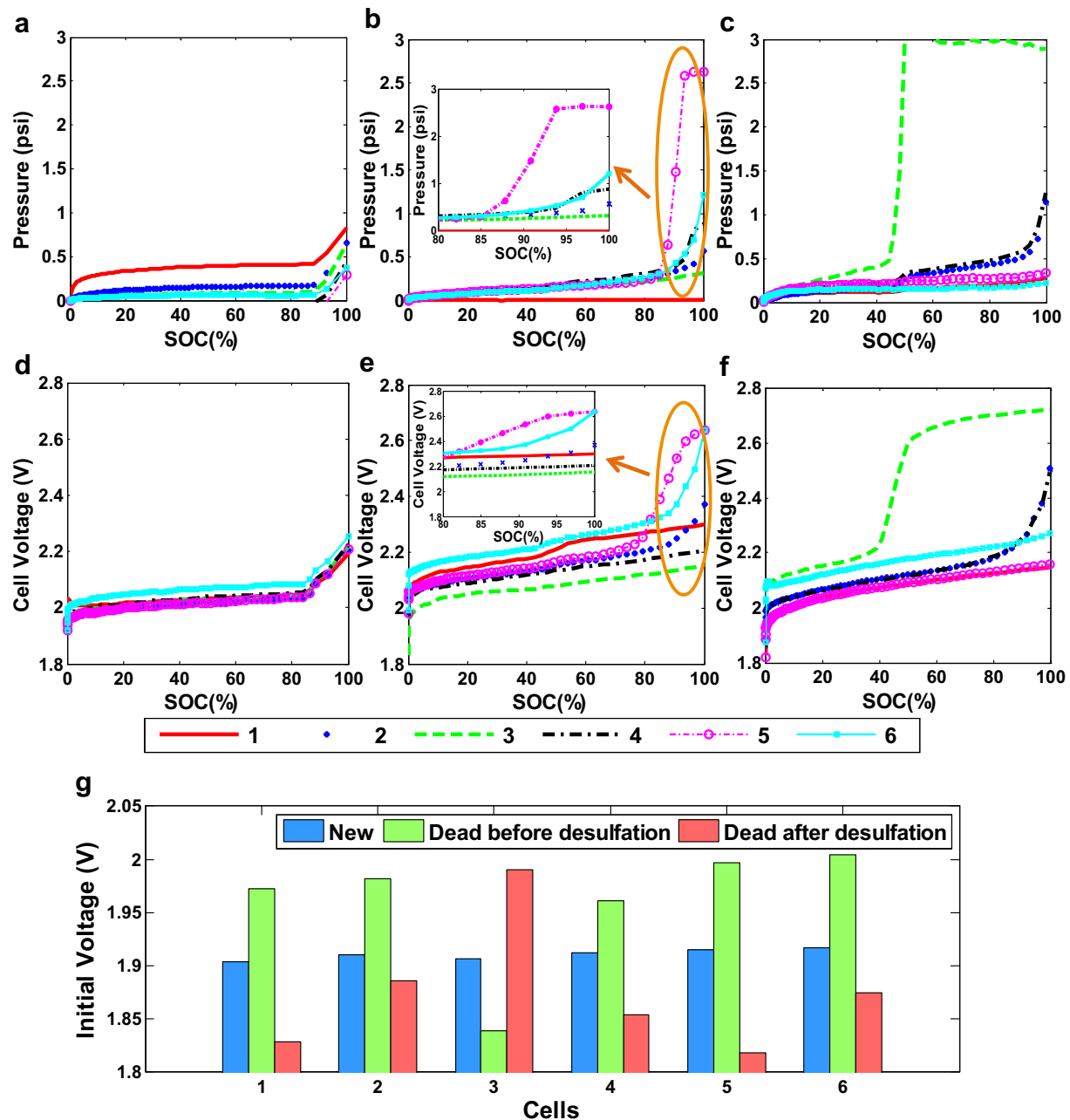


Fig. 5. Charge of the new and the dead batteries: (a) cell pressure of the new battery; (b) cell pressure of the dead battery before desulfation with inset showing the pressure build-up at the end of charge; (c) cell pressure of the dead battery after desulfation; (d) cell voltage of the new battery; (e) cell voltage of the dead battery before desulfation with inset showing voltage rise at the end of charge; (f) cell voltage of the dead battery after desulfation; (g) initial cell voltages of the new and the dead batteries before and after desulfation. (1 psi = 6.8948 kPa).

negative electrode. Then, the oxygen dissolves in the electrolyte and is reduced at the lead surface to produce water. Finally, the water is transported to the positive electrode to close the oxygen cycle [9,47–49]. The oxygen reduction efficiency relies heavily on the saturation level of the separator because a decrease in the saturation level leads to an increase in the void space in the separator [24]. Hence, when a VRLA battery ages, the saturation level is lowered due to multiple aging mechanisms and the oxygen cycle becomes more efficient. Similarly, hydrogen can be transported to the positive electrode, but the hydrogen recombination rate is very small due to poor kinetics that it can be neglected [50]. Therefore, no internal hydrogen cycle exists. When the cell is overcharged, gas evolution accelerates and excessive gas leaves the cell and if 100%

SOC is reached, the gas being released will ultimately consist of hydrogen and oxygen with a ratio of 2:1.

3.2. Desulfation charging algorithm

The optimal charging/desulfation algorithm is to direct all the charging current to the primary reaction, decomposing lead sulfate, using as large a current as possible but still suppressing the side reaction, gassing the most. The desulfation charging algorithm starts with constant-current (CC) charge to 2.40 V. At this point, the cell is close to full SOC. After that, the internal cell pressure, $P(t)$, is fed back to the controller to see if the pressure generation rate is within the tolerable range

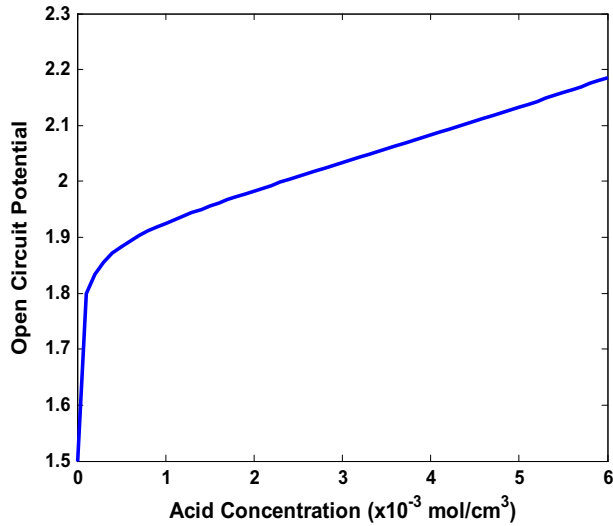


Fig. 6. Open circuit potential as a monotonically increase function of acid concentration.

($\dot{P} \cong \dot{P}_D = 6.8948 \text{ kPa day}^{-1} (1 \text{ psi day}^{-1})$). If the pressure rate is below the threshold value, the charging rate is increased. If the gassing process exceeds the pressure rate limit, meaning that too much current is going into a side reaction instead of recovering the cell capacity, the charging rate is decreased. In this way, the current used is as large as possible to convert sulfate but not gas to maximize the capacity recovered and the charge speed while minimizing gas generation. A PID controller ensures that the gassing pressure rate tracks $\dot{P}_D$. Conventional integral action is modified to account for the fact that the pressure within the cell cannot be decreased by discharge and the recombination and leaking rates that reduce pressure are very slow.

The objective of the desulfation control algorithm is to pump charge into the cells while minimizing water loss. Water loss is the number of moles of water that are converted to gas. Using the ideal gas law, the number of moles of gas produced is

$$n = \frac{\Delta PV}{RT} + n_{\text{leak}}, \quad (8)$$

where $\Delta P = P_{\text{atm}} + P_g - P_0$, V is the cell gas volume, R is the ideal gas constant, and T is temperature. The parameters R and V are constant and assumed to be constant, respectively. Atmospheric pressure P_{atm} and gauge pressure P_g change in time relative to the initial pressure P_0 . The cell chambers are not entirely sealed so gas leaks out with the approximate dynamics

$$\dot{n}_{\text{leak}} = \lambda P_g, \quad (9)$$

where λ is an experimentally determined rate constant. Using the measured P_g , P_0 , P_{atm} , and T and integrating Eq. (9), one can calculate and regulate the number of moles of gas produced using Eq. (8). For a sealed cell, if P_{atm} falls precipitously then P_g can rise and cause the cell to vent. After venting, P_0 is reset and desulfation continues.

3.3. Results and discussions

The experimental tests in Section 2 indicate that Cell #3 of the tested VRLA battery died of sulfation. To validate the test results and restore the capacity, Cell #3 is desulfated using the algorithm described in the previous section. Table 1 summarizes the desulfation test parameters. The four tests averaged 78.2 h and had an

Table 1
Desulfation test results.

Trial	Duration (h)	Charge acceptance	Charge speed (Ah h^{-1})
1	75	88.10%	0.289
2	94	97.93%	0.167
3	72	93.92%	0.175
4	72	97.73%	0.180

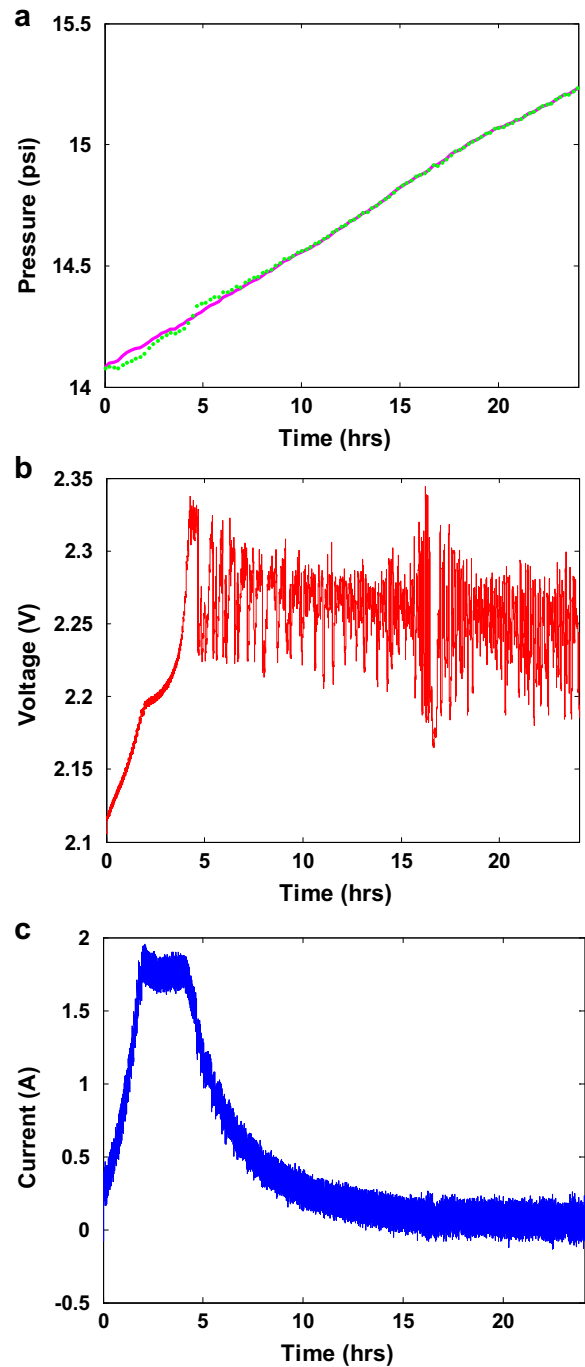


Fig. 7. Desulfation charge control experimental time response: (a) pressure, desired (magenta-solid) and measured (green-dotted); (b) voltage; and (c) current. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

average charging current of 0.2 A. The low charge acceptance of the first test indicates the conversion of hard sulfate to acid. The other three tests had higher charge acceptance, suggesting that the available sulfate had mostly been converted in the first iteration.

The three plots in Fig. 7 illustrated that the controller worked as expected. The two lines in Fig. 7(a) represented the allowable pressure generation and the actual pressure (both after compensated for temperature, atmosphere pressure and leaking). Fig. 7(b) and (c) displays the corresponding voltage and current. When started, the pressure generation rate was slower than the tolerance, thus the current was increased and the voltage rose accordingly. Until the pressure generation rate caught up the allowed rate, the current was oscillating around the 1.7 A so was the voltage because the pressure generation rate was swinging around the limit. After 5 h to the end of the test, the pressure generation rate passed the limit and the current was therefore attenuated to about 20–50 mA and the voltage was still oscillating around 2.25 V. This was possible the voltage threshold at which the gassing process occurred at the allowed rate as shown in Fig. 7(a).

Fig. 8 shows the measured cell capacity after each desulfation test. Over the course of four tests, the capacity increased from 39.9 Ah to 56 Ah, or a 41% increase in capacity. The first desulfation test showed the largest capacity gain of 11.6 Ah (29%). The second test yielded another 4 Ah (10%) increase in capacity. The small capacity drop after the third test is possibly due to measurement variation. Together, the third and fourth tests yielded only another 0.7 Ah (1.3%) increase in capacity. Further capacity changes were minimal, suggesting that other mechanisms, such as corrosion, may have become dominant. Alternatively, the lead sulfate crystals closest to the negative electrode may be harder than the outer layers, and therefore more difficult to break down. Although the capacity of the sulfated cell increased by 41%, the final cell capacity of 56.3 Ah was far from the nominal capacity of 88 Ah.

The full charge/discharge test shown in Figs. 4 and 5(c), (f) that the capacity of the battery increased 12 Ah (30%) from 40 Ah to 52.4 Ah. The increase in overall battery capacity is less than the increase observed in the sulfated cell alone, suggesting that a different cell may now be responsible for limiting the capacity of the battery. Fig. 4(e) and (f) shows that the shape of cell #3's voltage discharge curve after desulfation is similar to the other cells and no longer dramatically decreases before the other cells, as was observed before desulfation. Figs. 4 and 5(g) show that the desulfated cell's initial voltage is higher during both charge and discharge. This change is due to the fact that desulfation has converted more lead sulfate back into lead, lead dioxide, and sulfuric

acid, increasing the acid concentration. Both observations support the conclusion that that Cell #3 has been successfully desulfated. Fig. 5(c) and (f) shows that Cell #3 gases more easily after desulfation. The increase in acid concentration, and therefore cell voltage, may be responsible for causing for early gassing. A higher OCV during charging increases the overpotential inside the cell and promotes gassing.

4. Conclusions

EIS and pulse train responses reveal the non-uniformity among the cells in the aged battery and display the distribution of cell resistance and capacitance, indicating the relative health conditions of the cells.

The cause of death for VRLA batteries can be determined from a full charge/discharge cycle while monitoring individual cell pressures and voltages. In this study, Cells #2, #5, and #6 of a dead VRLA battery became overcharged and started gassing earlier than other cells during charge so the cause of death for these cells was dehydration. Cell #3 displayed a sharp, voltage drop during discharge, indicating death by sulfation.

The pressure rise associated with gassing was accompanied by a sharp rise in cell voltages. This suggests that individual cell pressure sensors may not be necessary to observe gassing.

A desulfation charging algorithm is implemented and proves that desulfation can partially reverse capacity loss, showing a 41% capacity increase in one cell of an aged VRLA battery and a 30% capacity increase overall. The results also validate the diagnosis of sulfation as an important aging mechanism, responsible for at least 33% of the capacity loss of this cell, or 25% of the capacity loss of the whole battery. The inability to restore the cell to its original capacity indicates that other aging mechanisms such as corrosion and water loss also contribute to aging. The tests show diminishing returns after 313 h of desulfation.

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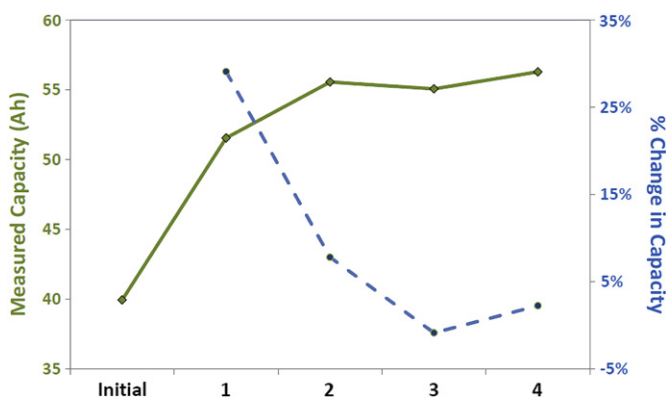


Fig. 8. Capacity after desulfation: measured cell capacity after each desulfation test, left (green-solid); percent of the change in cell capacity, right (blue-dashed). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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